Ligand Substitution Processes on Carbonylmetal Derivatives. 4.[1] NMR Study of the Reaction of Hydridocarbonylchromates with PX_3 (X = Br, Cl)[†]

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Summary: At 193 K, $K^+[HCr(CO)_5]^-$ (1 equiv) reacts with PBr_3 to give $Cr(CO)_5PH_3$ and $K^+[BrCr(CO)_5]^-$. The latter further reacts with PBr_3 only above 253 K to give $Cr(CO)_5PBr_3$. At room temperature, $K^+[HCr(CO)_5]^-$ (3 equiv) reacts with PBr_3 to give $Cr(CO)_5PH_3$ as the sole phophorus derivative. A similar reactivity is observed for the reaction of $K^+[HCr(CO)_5]^-$ with PCl_3. In contrast, $K^+(\mu\text{-}H)[Cr(CO)_5]_2^-$ reacts with PBr_3 only above 298 K, affording selectively $Cr(CO)_5PBr_3$.

Ligand substitution processes in transition metal complexes, especially neutral metal carbonyls, have attracted much attention, both for the design of specific syntheses of heteroleptic complexes and for a contribution to the understanding of reaction mechanisms, particularly the loss of small molecules or ions from low-valent metal complexes.[2−4]

In the last years, our study of ligand substitution processes on $K^+[HFe(CO)_4]^-$ has been particularly fruitful, both from a synthetic point of view and for the understanding of the reactivity of hydridocarbonylferrates toward phosphites and phosphines.[5]

More recently we reported a study of the reaction of phosphines with the chromium derivative $K^+[HCr(CO)_5]^-$, **1**, in aprotic solvents.[1] The reaction of **1** with PEt_3 starts by a carbonyl ligand substitution, generating the monosubstituted derivative $K^+[HCr(CO)_4PEt_3]^-$. Although the latter complex could be spectroscopically characterized, it reacts in situ with the PEt_3 to afford the disubstituted *trans*-$Cr(CO)_4(PEt_3)_2$ complex by displacement of the hydride ligand (eqs 1, 2).

$$\underset{\mathbf{1}}{K^+[HCr(CO)_5]^-} + PEt_3 \xrightarrow{THF} K^+[HCr(CO)_4(PEt_3)]^- + CO \quad (1)$$

$$K^+[HCr(CO)_4PEt_3]^- + PEt_3 \xrightarrow{THF} Cr(CO)_4(PEt_3)_2 + KH \quad (2)$$

The bridged dinuclear hydride $K^+(\mu\text{-}H)[Cr(CO)_5]_2^-$, **2**, also reacts with PEt_3 to give *trans*-$Cr(CO)_4(PEt_3)_2$ (eq 3).[1,6]

$$\underset{\mathbf{2}}{K^+(\mu\text{-}H)[Cr(CO)_5]_2^-} + 4\ PEt_3 \xrightarrow{THF} 2\ Cr(CO)_4(PEt_3)_2 + KH \quad (3)$$

Thus, although different mechanisms are involved,[1] the reactions of **1** and **2** with PEt_3 yield the same disubstituted *trans*-$Cr(CO)_4(PEt_3)_2$ derivative.

In this communication, we wish to report for the first time the reactions of **1** and **2** with trihalogenophosphines, PX_3 (X = Br, Cl), evidencing a great difference of reactivity between these two hydridocarbonylmetalates.

When **1** was reacted with 1 equiv of PBr_3 in THF at RT for 3 h in a Schlenk tube, a mixture of two new phosphorus complexes is formed which exhibits $^{31}P\{^1H\}$ NMR signals at $\delta = -127.7$ and 95.8 ppm (ca. 1:2 ratio). PBr_3 ($\delta = 233.8$ ppm) was totally consumed. According to the assignments determined later (vide infra), this reaction can be represented by eq 4.

$$\underset{\mathbf{1}}{K^+[HCr(CO)_5]^-} + PBr_3 \xrightarrow[RT]{THF} 1/3\ \underset{\mathbf{3}}{Cr(CO)_5PH_3} + 2/3\ \underset{\mathbf{4}}{Cr(CO)_5PBr_3} + KBr \quad (4)$$

To gain more information, the reaction of **1** with PBr_3 was performed at low temperature in THF-d_8 in a NMR tube and monitored by ^{31}P and ^1H NMR. After mixing the precooled reagents (1:1) at ca. 100 K, the temperature of the probe was allowed to reach 193 K. After 0.5 h, the ^{31}P NMR spectrum indicated the presence of unreacted PBr_3 (major compound) and of a unique new phosphorus compound, **3**, exibiting a well-defined quadruplet at $\delta = -127.7$ ppm ($^1J_{P-H} = 344$ Hz). No trace of free PH_3 ($\delta_P = -242.4$ ppm) could be detected. The ^1H NMR spectrum indicated the total consumption of **1** ($\delta = -6.9$ ppm) and the appearance of a doublet at $\delta = 3.8$ ppm ($^1J_{H-P} = 344$ Hz) corresponding to **3** (a small

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(1) Part of the Ph.D. Thesis of E. Roblou. For Part 3, see: Brunet, J.-J.; Diallo, O.; Donnadieu, B.; Roblou, E. *Organometallics* **2002**, *21*, 3388−3394.

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signal corresponding to **2** ($\delta = -19.5$ ppm) is also observed). Examination of literature data led us to conclude that **3** was the previously reported monosubstituted complex $Cr(CO)_5PH_3$.[7] This assignment was confirmed by the ^{13}C NMR spectrum of the reaction mixture at 193 K.[8] Interestingly, the above ^{13}C NMR spectrum also indicates the presence of $K^+[BrCr(CO)_5]^-$, **5**, and of small amounts of **2**, both identified by comparison with the ^{13}C NMR spectra of authentic samples registered at 193 K.[9] Furthermore a very minor signal is observed at $\delta = 215.5$ ppm. The latter does not correspond to $Cr(CO)_5$thf [10] and may be tentatively assigned to $K^+(\mu\text{-Br})[Cr(CO)_5]_2^-$.[13] These observations are *qualitatively* summarized by eq 5.

$$\underset{\mathbf{1}}{K^+[HCr(CO)_5]^-} + PBr_3 \xrightarrow[193\ K]{THF} \underset{\mathbf{3}}{Cr(CO)_5PH_3} + \underset{\mathbf{5}}{K^+[BrCr(CO)_5]^-} \quad (5)$$

Since the reaction did not seem to evolve at 193 K, the temperature was allowed to increase slowly. ^{31}P NMR monitoring allowed the observation of the formation of a new phosphorus complex, **4** ($\delta = 95.8$ ppm, s), starting when the temperature reached ca. 255 K, whereas the consumption of **2** apparently occurred only after reaching 273 K (^1H NMR analysis). Consumption of PBr_3 was complete at 293 K. The ^{31}P NMR chemical shift of **4** corresponds to that of the monosubstituted $Cr(CO)_5PBr_3$ derivative.[14] This assignment was confirmed by recording the ^{13}C and $^{13}C\{^{31}P\}$ NMR spectra of pure **4** (vide infra), which exhibits two doublets (ca. 1:4 ratio) ($\delta_{trans-CO} = 217.8$ ppm, d, $^2J_{C-P} = 5$ Hz, and $\delta_{cis-CO} = 213.3$ ppm, d, $^2J_{C-P} = 14$ Hz,), in agreement with literature data.[14]

It thus appeared that **1** reacts with PBr_3 at 193 K to give selectively **3**, with formation of unsaturated "$Cr(CO)_5$" species, stabilized mainly as **5**. In contrast, in situ generated **2** does not react with PBr_3 at 193 K. The reaction starts only at higher temperatures to give $Cr(CO)_5PBr_3$, **4** (and perhaps some amounts of **3**). Furthermore, it could be anticipated that PBr_3 reacts with $K^+[BrCr(CO)_5]^-$ near 255 K, affording **4**.

To verify the above hypothesis, we examined the reaction of PBr_3 with **5**.[15] The reaction of PBr_3 with **5** (1 equiv) in THF was started at 193 K and monitored by ^{31}P NMR. As expected, no reaction occurred at this temperature. Allowing the temperature to increase slowly promoted the formation of **4** near 255 K, thus confirming our previous expectations. The consumption of PBr_3 was complete after a few hours at 298 K.

Owing to the formation of $Cr(CO)_5PH_3$ (eq 1), we also adapted the stoichiometry for the reaction of **1** with PBr_3. Reacting PBr_3 with 3 equiv of **1** in THF-d_8 at RT for 0.25 h promoted the total consumption of **1** (^1H NMR analysis) and the formation of **3** as the sole phosphorus complex (^{31}P NMR analysis), thus suggesting a quantitative transformation (eq 6). The liberated "$Cr(CO)_5$" moeity is stabilized as **5** (^{13}C NMR analysis).

$$3\underset{\mathbf{1}}{K^+[HCr(CO)_5]^-} + PBr_3 \xrightarrow[0.25\ h]{THF,\ RT} \underset{\mathbf{3}}{Cr(CO)_5PH_3} + 2\ \underset{\mathbf{5}}{K^+[BrCr(CO)_5]^-} + KBr \quad (6)$$

To try to detect some intermediate species, reaction 6 was performed using a large (100 fold) excess of PBr_3. Unfortunately, even at 193 K, no intemediate could be evidenced. In particular, no trace of free PH_3 could be detected. Consequently, we also examined the reaction of PH_3 with **5**. Bubbling slowly gaseous PH_3[18] into a THF solution of **5** at 193 K clearly indicated (^{31}P NMR and IR monitoring) that no reaction occurred at this temperature. The reaction of PH_3 with **5** started only when the temperature reached 293 K, generating **3** selectively. It thus appears that the formation of **3** at 193 K (reaction 5) does not involve free PH_3.

Although a little less reactive than PBr_3, PCl_3 similarly reacts with **1** to give **3**. Interestingly, however, when the reaction of **1** with a 100-fold excess of PCl_3 was conducted in *toluene* at RT, ^{31}P and ^1H NMR analyses allowed the observation of two intermediate carbonylchromium complexes, $Cr(CO)_5PHCl_2$ and $Cr(CO)_5PH_2Cl$.[19] This result confirms that PH_3 is not formed before complexation on the carbonylchromium species and strongly suggests that the reaction starts by a tandem reduction−complexation of PCl_3 generating $Cr(CO)_5PHCl_2$, which is further reduced, step by step, to $Cr(CO)_5PH_3$.

For comparison, we also examined the reaction of **2** with PBr_3. Adding PBr_3 (1 equiv) to a THF-d_8 solution of **2** at 193 K in a NMR tube confirmed that **2** does not react with PBr_3 at this temperature (^{31}P NMR analysis). The reaction started only when the temperature reached 293 K, affording selectively **4** (no trace of **3**). PBr_3 was

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[7] The reported ^{31}P NMR chemical shift for **3** is $\delta_P = -129.6$ ppm. The disubstituted *cis*-$Cr(CO)_4(PH_3)_2$ has also been described ($\delta_P = -121.5$ ppm, $\delta_H = 3.7$ ppm, $^1J_{H-P} = 317$ Hz). Moser, E.; Fischer, E. O.; Bathelt, W.; Gretner, W.; Knauss, L.; Louis, E. *J. Organomet. Chem.* **1969**, *19*, 377−385.

[8] The $^{13}C\{^1H\}$ NMR spectrum of **3** exhibits two doublets in a 1:4 ratio ($\delta_{trans-CO}$ 221.6 ppm, $^2J_{C-P} = 6$ Hz and δ_{cis-CO} 216.6 ppm, $^2J_{C-P} = 14$ Hz).

[9] ^{13}C NMR for **5** (THF-d_8 at 193 K): $\delta_{trans-CO}$ 225.0 ppm and δ_{cis-CO} 217.2 ppm. ^{13}C NMR for **2** (THF-d_8 at 193 K): $\delta_{trans-CO}$ 226.1 ppm and δ_{cis-CO} 221.3 ppm.

[10] The ^{13}C NMR data of $Cr(CO)_5$thf have never been reported, probably because of its high instability in solution.[11] A solution of $Cr(CO)_6$ in THF-d_8 was irradiated for 1 h at $\lambda = 365$ nm. The IR spectrum of the above solution exhibits the expected main absoption bands (1936 and 1894 cm^{-1})[12] together with that of unreacted $Cr(CO)_6$ (1977 cm^{-1}). The solution was immediadely cooled to ca. 193 K and the ^{13}C NMR spectrum recorded at 193 K for 3 h. It exhibits signals at δ 212.9 ppm ($Cr(CO)_6$) and δ 220.8 ppm, tentatively assigned to the *cis*-CO of $Cr(CO)_5$thf.

[11] Brown, R. A.; Dobson, G. R. *Inorg. Chim. Acta* **1972**, *6*, 65−71.

[12] Arndt, L. W.; Bischoff, C. J.; Darensbourg, M. Y. *Inorg. Synth.* **1989**, *26*, 335−341.

[13] Ruff, J. K. *Inorg. Chem.* **1968**, *7*, 1821−1825.

[14] Davies, M. S.; Pierens, R. K.; Aroney, M. J. *J. Organomet. Chem.* **1993**, *458*, 141−146.

[15] Although $[XCr(CO)_5]^-$ derivatives have been known for long time,[16] the potassium salt $K^+[BrCr(CO)_5]^-$, **5**, has never been described. Its preparation was adapted from that of $Et_4N^+[BrCr(CO)_5]^-$ by reacting **1** with $CHBr_3$ in THF.[17] ^{13}C NMR spectrum of **5** at 193 K (THF-d_8): 2 signals in 1:4 ratio, $\delta_{trans-CO}$ 225.0 ppm and δ_{cis-CO} 217.2 ppm.

[16] Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068−2070.

[17] Gibson, D. H.; Ahmed, F. U.; Phillips, K. R. *Organometallics* **1982**, *1*, 679−681.

[18] PH_3 was generated by reaction of PCl_3 with $LiAlH_4$ according to: Gunn, S. R.; Green, L. G. *J. Phys. Chem.* **1961**, *65*, 779−783.

[19] NMR data (toluene-d_8) for $Cr(CO)_5PHCl_2$: ^{31}P, δ 158.8 ppm, d, $^1J_{P-H} = 402$ Hz; ^1H, δ 7.63 ppm, d, $^1J_{H-P} = 402$ Hz, in agreement with literature data.[20] NMR data (toluene-d_8) for $Cr(CO)_5PH_2Cl$: ^{31}P, δ 51.2 ppm, t, $^1J_{P-H} = 356$ Hz; ^1H, δ 5.68 ppm, d, $^1J_{H-P} = 356$ Hz.

[20] Bartmann, A.; Diemert, K.; Kuchen, W. *J. Organomet. Chem.* **1993**, *453*, 65−70.

totally converted after 10 h at 293 K, whereas large amounts of **2** were still present. As expected, reacting **2** with 2 equiv of PBr_3 for 23 h at RT (eq 7) induced complete consumption of PBr_3 with formation of **4** as the sole carbonylchromium complex (^{13}C NMR analysis).

$$\underset{\mathbf{2}}{K^+(\mu\text{-H})[Cr(CO)_5]_2^-} + 2\ PBr_3 \xrightarrow[293\ K]{THF} \underset{\mathbf{4}}{Cr(CO)_5PBr_3}\ KH \quad (7)$$

It is thus clear that **1** and **2** react quite differently with PX_3. The reaction of **1** may be viewed as a fast tandem reduction−complexation of PX_3 by the hydride, generating $Cr(CO)_5PHX_2$, which is further reduced by **1**, to finally afford $Cr(CO)_5PH_3$. The liberated "$Cr(CO)_5$" species are stablized as $K^+[XCr(CO)_5]^-$.

In contrast, **2** does not react with PBr_3 as a hydride transfer agent. Therefore, it would be expected to react like classical phosphines. Under the same conditions, **2** has been shown to react with PEt_3 to afford the disubstituted derivative $Cr(CO)_4(PEt_3)_2$, a reaction that involves the substitution of both a CO *and* the hydride ligand.[1,6] The reaction of **2** with PBr_3 involves a completely different mechanism. Indeed, no CO substitution is observed in the final product, and the in situ disruption of **2** into "$Cr(CO)_5$" and $[HCr(CO)_5]^-$ is highly doubtful since the latter would have reacted with PBr_3 to give $Cr(CO)_5PH_3$ and $Cr(CO)_5PBr_3$ according to eq 4.

Work is in progress to gain more insight into the reaction mechanism of $K^+(\mu\text{-H})[Cr(CO)_5]_2^-$ with trihalophosphines.

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